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(54) **TRANSPARENT SYNTHETIC RESIN LAMINATE HAVING PHOTOCHROMISM**

(57) A transparent synthetic resin laminate with photochromism property consisting essentially of two transparent synthetic resin layers and a photochromic layer formed by curing a mixture of a two liquid polyurethane

of a polyurethane prepolymer and a curing agent and a photochromic organic compound which is interposed between said two transparent synthetic resin layers.

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## Description

## FIELD OF ART

5 [0001] The present invention relates to a transparent synthetic resin laminate with photochromism property and specifically, to a transparent synthetic resin laminate with photochromism property for use of an optical lens which is excellent in both control of thickness of a photochromic coated film and surface smoothness thereof and exhibits a high color development speed and a high color disappearance speed.

## 10 BACKGROUND OF THE INVENTION

[0002] As conventional optical lenses, particularly, photochromic lenses, inorganic lenses have generally spread. That is, it was usual to add an inorganic coating layer with photochromism property to a surface of a glass or a curing plastic such as CR-39. Recently, as a lens itself, plastic lenses with high impact resistance have spread. Particularly, in United States of America, polycarbonate lenses have widely spread and demand for a sun glass with impact resistance has suddenly increased because of extensive outdoor activities.

[0003] As synthetic resin laminates with photochromism property, hitherto, a laminate obtained by adding a photochromic organic compound to a silicone surface curing coating agent and then coating it on one side of a substrate and then performing cure and a laminate obtained by adding a photochromic organic compound to an urethane coating agent and then coating it on one side of a synthetic resin laminate and then performing cure have been known (Japanese Patent Kokai (Laid-open) No.63-178193).

[0004] However, in the process for coating a coating agent containing a photochromic organic compound on one side of a synthetic resin substrate, it was difficult to obtain a smooth coated film surface and to control a thickness of a coated film. Thus, when a coated film surface is not smooth, it is not practically preferable since use of the laminate as a photochromic lens causes distortion through the lens.

[0005] Further, Japanese Patent Kokai (Laid-open) No.61-148048 discloses a photochromic laminate interposed a photochromic layer containing a spironaphth oxazine derivative between transparent material layers. Although the prior art discloses an example in which one liquid type polyurethane resin is contained in a photochromic layer, both a color development speed and a color disappearance speed are low, and thus insufficient.

[0006] Moreover, also in photochromic lenses, various process such as direct kneading into a resin and coating on a resin surface were tried. However, they are not yet put into practice because of development shortage in performances due to insufficient heat resistance of photochromic elements during kneading and, also in surface coating, contrast shortage from limitation of coated film thickness.

[0007] Thus, in a present situation, there is obtained no transparent synthetic resin laminate with photochromism property as a photochromic lens in which both a color development speed and a color disappearance speed are high and surface smoothness of a coated film and control of coated film thickness in a photochromic layer are excellent.

## DISCLOSURE OF THE INVENTION

40 [0008] The present invention solves the above-mentioned prior art problems. An object of the present invention is to provide a transparent synthetic resin laminate with photochromism property in which both a color development speed and a color disappearance speed are high and contrast in color development is maintained for a long time and surface smoothness of a coated film and control of thickness of a coated film in a photochromic layer are excellent.

[0009] Under such situation, as a result of studies of the above-mentioned prior art problems, the inventors have found that there is obtained a transparent synthetic resin laminate in which both a color development speed and a color disappearance speed are high and contrast in color development is maintained for a long time and surface smoothness of a coated film and control of thickness of a coated film in a photochromic layer are excellent by interposing a photochromic layer formed by curing a mixture of a two-liquid type polyurethane of a polyurethane prepolymer and a curing agent, a photochromic organic compound, a light stabilizer and an antioxidant between two transparent synthetic resin layers, and have accomplished the present invention.

[0010] That is, the present invention provides a transparent synthetic resin laminate with photochromism property consisting essentially of two transparent synthetic resin layers and a photochromic layer formed by curing a mixture of a two liquid polyurethane of a polyurethane prepolymer and a curing agent and a photochromic organic compound and further a light stabilizer and an antioxidant which is interposed between said two transparent synthetic resin layers.

[0011] Further, the present invention provides a process for producing a transparent synthetic resin laminate with photochromism property which comprises:

coating a mixture of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent, a photochromic

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organic compound and a solvent and further a light stabilizer and an antioxidant on one side of a transparent synthetic resin sheet.

then, removing the solvent from the mixture to a state not to contain substantially the solvent, and then, adhering another transparent synthetic resin sheet to the coated side of said synthetic resin sheet, and

5 then, curing the two-liquid polyurethane, thereby, forming a photochromic layer.

[0012] The present invention will be described in detail below.

[0013] The transparent synthetic resin to be used in the present invention is not limited as long as it is a resin with high transparency. It is preferable to use a polycarbonate resin and a polymethylmethacrylate resin. As the combination of two transparent synthetic resins, a polycarbonate resin, a polymethylmethacrylate or both thereof is applied to each of two transparent synthetic resins. A transparent synthetic resin with a thickness of 50 to 2000  $\mu\text{m}$  is used. Particularly, when bending processing into a lens form is performed, it is preferable to use a synthetic resin sheet with a thickness of 100 to 1000  $\mu\text{m}$ .

10 [0014] In the present invention, there is provided a photochromic layer formed by cure of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent containing a photochromic organic compound, a light stabilizer and an antioxidant which is interposed between two transparent synthetic resin layers. Thereby, it becomes possible to produce industrially a transparent synthetic resin laminate excellent in both heat resistance and impact resistance which exhibits a high color development speed and a high color disappearance speed in use as a lens and possesses 20 photochromic performance excellent in surface smoothness of a coated film in a photochromic layer equivalent to conventional inorganic type and maintains a photochromic characteristics such as contrast in color development for a long time.

25 [0015] Generally, polyurethane includes one-liquid type and two-liquid type. In the present invention, it is preferable to use a two-liquid polyurethane of a polyurethane prepolymer and a curing agent from the aspects of color development speed and color disappearance speed and solubility of photochromic compound and various additives. Actually, a prepolymer is dissolved in a specific solvent and mixed with various additives including a photochromic compound and then a curing agent is added thereto.

30 [0016] As the polyurethane prepolymer, a compound obtained by reaction of isocyanate and polyol in a specific proportion is used. That is, the polyurethane prepolymer is a compound with an isocyanate group on both ends obtained from diisocyanate and polyol. As the diisocyanate compound to be used for the polyurethane prepolymer, diphenylmethane-4,4'-diisocyanate (MDI) is preferable. Further, as the polyol, it is preferable to use polypropylene glycol (PPG) with a polymerization degree of 5 to 30.

35 [0017] The molecular of the polyurethane prepolymer is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

[0018] On the other hand, the curing agent is not limited as long as it is a compound with two hydroxyl groups. Examples of the curing agent include polyurethane polyol, polyether polyol, polyester polyol, acryl polyol, polybutadiene polyol and polycarbonate polyol, among which polyurethane polyol with a hydroxyl group on its end obtained from specific isocyanate and specific polyol is preferable. Particularly, polyurethane polyol with a hydroxyl group on at least 40 both ends derived from diisocyanate and polyol is preferable and it is preferable to use tolylenediiisocyanate (TDI) as the diisocyanate. Further, as the polyol, it is preferable to use PPG with a polymerization degree of 5 to 30.

[0019] The molecular weight of the curing agent is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

[0020] In order to adjust the viscosity of the polyurethane prepolymer and the curing agent, a solvent such as ethyl acetate and tetrahydrofuran may be used.

45 [0021] In the present invention, the organic compound with photochromic property is not limited as long as it has good compatibility with the polyurethane prepolymer. Photochromic organic compound obtainable on the market can be used. As the photochromic organic compound, spiropyran compounds, spiroxazine compounds and naphthopyran compounds are preferably used from the aspect of photochromic performance.

50 [0022] Examples of the spiropyran compound include 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], 1',3',3'-trimethylspiro-8-nitro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-6-hydroxyspiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethylspiro-8-methoxy(2H-1-benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline), 6,8-dibromo-1',3',3'-trimethylspiro(2H-1-benzopyran-2,2'-indoline), 6-ethoxy-1',3',3',4',7'-pentamethylspiro(2H-1-benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethylspiro-6,8-dinitro(2H-1-benzopyran-2,2'-indoline), 1',3,3-triphenylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 3,3,1-diphenyl-3H-naphtho(2,1-b)pyran, 1,3,3-triphenylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2-methoxy-5-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2-naphthylmethyl)-3,3-dimethylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran] and 1,3,3-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-indole).

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[0023] Examples of the spirooxazine compound include 1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-methoxy-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-chloro-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 4,7-diethoxy-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1,3,3,5-tetramethyl-9'-ethoxyspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-ber zyl-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-methoxybenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(2-methylbenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-chlorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-bromobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1,3,5,6-tetramethyl-10

9'-ethoxyspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-ber zyl-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(3,5-dimethylbenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-chlorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-bromobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1,3,5,6-tetramethyl-10-oxazine], 1-(2-fluorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(3,5,6-pentamethylspiro [indoline-2,3'-[3H] pyrido 3-ethylspiro [indoline-2,3'-[3H] pyrido [3,2-f] [1,4]-benzoxazine], 1,3,3,5,6-pentamethylspiro [2H-indole-2,3'-[3H] [3,2-f] [1,4]-benzoxazine], 6'-2,3-dihydro-1H-indole-1-yl]-1,3-dihydro-3,3-dimethyl-1-propyl-spiro [2H-naphtho [2,1-b] [1,4] oxazine], 6'-2,3-dihydro-1H-indole-1-yl]-1,3-dihydro-3,3-dimethyl-1-(2-methylpropyl)-spiro [2H-indole-2,3'-[3H]- naphtho [2,1-b] [1,4] oxazine], 1,3,3-trimethyl-1-8'-2,3-dihydro-1H-indole-1-yl)-spiro [2H-indole-2,3'-[3H]- naphtho [2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-1-piperidinyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-1-piperidinyl)-6-(trifluoromethyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine] and 1,3,3,5,6-pentamethyl-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine].

[0024] Examples of the naphthopyran compound include 3,3-diphenyl-3H-naphtho [2,1-b] pyran, 2,2-diphenyl-2H-naphtho [1,2-b] pyran, 3-(2-fluorophenyl)-3-(4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, 3- (2-methyl-4-methoxyphenyl)-3-(4-ethoxyphenyl)-3H-naphtho [2,1-b] pyran, 3-(2-furil)-3-(2-fluorophenyl)-3H-naphtho [2,1-b] pyran, 3-(2-thienyl)-3-(2-fluoro-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran 3-(2-(1-methylpyrrolidinyl)-3-(2-methyl-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, spiro [bicyclo [3.3.1] nonane-9,3'-3H-naphtho [2,1-b] pyran], spiro [bicyclo [3.3.1] nonane-9-2'-3H-naphtho [2,1-b] pyran], 4-[4-[6-(4-morpholinyl)-3-phenyl-3H-naphtho [2,1-b] pyran-3-yl] phenyl]-morpholine, 4-[3-(4-methoxyphenyl)-3-phenyl-3H-naphtho [2,1-b] pyran-6-yl]-morpholine, 4-[3-3-bis(4-methoxyphenyl)-3H-naphtho [2,1-b] pyran-6-yl]-morpholine, 4- [3-phenyl-3- [4-(1-piperidinyl) phenyl]-3H-naphtho [2,1-b] pyran-6-yl]-morpholine and 2,2-diphenyl-2H-naphtho [2,1-b] pyran.

[0025] In order to ensure the life of the synthetic resin laminate of the present invention, it is necessary to add various stabilizers. As the stabilizer, light stabilizers such as hindered amine and antioxidants such as hindered phenol are added.

[0026] Examples of hindered amine include bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-[(3,5-bis(1,1-dimethylethyl)][4-hydroxyphenyl] methyl] butyl malonate, 1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate, 1-[2-(3-(3,5-di-t-butyl-4-hydroxy-phenyl) propionyloxy)ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy]-2,2,6,6-tetramethylpiperidine, 4-benzoxyloxy-2,2,6,6-tetramethylpiperidine, triethylenediamine and 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro [4,5]decane-2,4-dione. As other nickel ultraviolet ray stabilizer, [2,2'-thiobis(4-t-octylphenolate)]-n-butylamine nickel, [4,5]decane-2,4-dione. As other nickel ultraviolet ray stabilizer, [2,2'-thiobis(4-t-octylphenolate)]-n-butylamine nickel, nickel complex-3,5-di-t-butyl-4-hydroxybenzyl · phosphoric acid monoethylate and nickel · dibutyl carbamate also can be used. Particularly, as hindered amine light stabilizer, bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate or a condensation product of 1,2,2,6,6-pentamethyl-4-piperidinol, tridodecyl alcohol and 1,2,3,4-butanetetra carboxylic acid as tertiary hindered amine compound is preferable.

[0027] Examples of the antioxidant include 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, 2,2'-methylenebis(4-ethyl-6-t-butylphenol), tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate]methane, 2,6-di-t-butyl-p-cresol, 4,4'-butyldenebis(3-methyl-6-t-butylphenol), 1,3,5-tris(3', 5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H, 3H, 5H) trione, stearyl-β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanuric acid, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene.

[0028] Particularly, as phenol antioxidant, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, tetrakis-(methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate) methane and 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione which contain 3 or above of hindered phenol are preferable.

[0029] The transparent synthetic resin laminate with photochromic property of the present invention is produced according to below process. A photochromic organic compound is added in the proportion of 0.2 to 5 % to resin solid matter to a solution of a polyurethane prepolymer diluted with specific organic solvent and an additive(s) of hindered amine light stabilizer and/or antioxidant is (are) further added thereto in the proportion of 0.1 to 5 % to resin solid matter and uniformly mixed with stirring. Then, a curing agent is further added thereto in a 1/H ratio of isocyanate group (I) to hydroxyl group (H) of the curing agent of 0.8 to 20 and preferably 1 to 10 as a standard and stirring is further performed to form a solution. It is suitable that the polymer concentration in the solution thus obtained is usually 40 to 90 % by weight. The solution is coated with a doctor blade of coating thickness 100 to 1000 μm on one side of a transparent synthetic resin sheet. After the completion of coating, heat drying is performed to the state substantially not containing

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the solvent on the coated surface and another transparent synthetic resin sheet is adhered to the coated surface of said synthetic resin sheet in a sandwich form. The above-mentioned heat drying is usually performed at 20 to 50 °C for 5 to 60 minutes. A laminate sheet thus obtained is heated to cure the polyurethane prepolymer containing the curing agent, whereby a transparent synthetic resin laminate is obtained. The curing conditions of the polyurethane prepolymer are usually 60 to 140 °C and 2 hours to 1 week.

5 [0030] Examples of the solvent include hydrocarbons such as hexane, heptane, octane, cyclohexane, toluene, xylene and ethyl benzene, esters such as ethyl acetate, methyl acetate, isopropyl acetate, n-propyl acetate, isobutyl acetate, n-butyl acetate, isoamyl acetate, methyl propionate and isobutyl propionate, ketones such as acetone, methylethyl ketone, diethyl ketone, methylisobutyl ketone, acetyl acetone and cyclohexyl ketone, ether esters such as cellosolve acetate, diethylglycol acetate, ethyleneglycol mono n-butylether acetate, propylene glycol and monomethylether acetate, tertiary alcohols such as diacetone alcohol and t-amy1 alcohol and tetrahydofuran. Particularly, ethyl acetate, tetrahydofuran and toluene are preferable.

## BEST MODE FOR CARRYING OUT THE INVENTION

15 [0031] The present invention will be described in more detail below referring to Examples, which are not intended to limit the scope of the present invention.

## Examples 1 to 4

20 [0032] 2 % of Photochromic compound 1 or 2 to resin solid matter and 1 to 2 % of Additive 1 to resin solid matter were dissolved in a solution of 15 g of a polyurethane precursor having a NCO group equivalent weight (equivalent weight : average molecular weight per one functional group) of 1500 obtained by reaction of diphenylmethane-4,4'-diisocyanate and polypropylene glycol having an average polymerization degree of 15 diluted with 8.3 g of tetrahydrofuran and stirred until uniformity was ensured and then 3 g of a curing agent having a hydroxyl group equivalent weight of 1050 obtained by reaction of tolylene diisocyanate and polypropylene glycol having an average polymerization degree of 10 was added thereto and further stirred.

25 [0033] The solution thus obtained was coated with a doctor blade of coating thickness 400 µm, manufactured by Mitsubishi Seiki K.K., in Japan on a polycarbonate film of thickness 700 µm (trade name : IUPILON, manufactured by Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer and the polycarbonate film was adhered to make a sheet form and then heat curing was performed at 70 °C for 2 days. The measurement of the transmittance in maximum absorption wave length and the evaluation of the light resistance for the synthetic resin laminate thus obtained were performed and the thickness of the photochromic layer was measured and its appearance was observed. The proportion of each component for the formation of the laminates was shown in Table 1. The evaluation results of the laminated were shown in Table 2.

## Photochromic compound 1 :

30 [0034] 1,3-dihydro-1,3,3,5,6 (1,3,3,4,5) pentamethyl-spiro[2H-indole-2,3-[3H]-naphtho[2,b] [1,4]oxazine]

## Photochromic compound 2 :

35 [0035] 9,3-diphenyl-3H-naphtho[2,1-b]pyran

## Additive 1 :

40 [0036] bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate

[0037] Each performance was evaluated according to the following methods.

## [Measurement of transmittance]

45 [0038] A single wave length light of 360 nm was irradiated with an ultramonomochromatic light source and transmittance after 5 minutes from the starting of the irradiation and transmittance in non-irradiation were measured. A spectrophotometer, manufactured by Nihon Bunko k.k., in Japan was used in the measurement of transmittance and the transmittance in maximum absorption wave length was measured.

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## [Evaluation of light resistance]

[0039] Contrast prior to exposure and contrast after exposure for 60 hours to a sunshine weather meter under below conditions were measured. In order to compare with contrast prior to exposure, contrast retention percentage was calculated to evaluate its life.

## (1) Setting conditions of sunshine weather meter

- Irradiance : 255 w/m<sup>2</sup> (300 to 700 nm)
- Temperature : room temperature
- Rainfall was not applied.

## (2) Calculation of contrast retention percentage (%)

15 Contrast retention percentage (%)

$$= (L^*_3 - L^*_4) \times 100 / (L^*_1, L^*_2)$$

20

- $L^*_1$  : contrast prior to light resistance test (in ultraviolet light non-irradiation)
- $L^*_2$  : contrast prior to light resistance test (in ultraviolet light irradiation)
- $L^*_3$  : contrast after light resistance test (in ultraviolet light non-irradiation)
- $L^*_4$  : contrast after light resistance test (in ultraviolet light irradiation)

## 25 (3) Evaluation

[0040] Contrast life was evaluated based on the following criterion

30

- : contrast retention percentage after light resistance test is 70 %, or above.
- △ : contrast retention percentage after light resistance test is below 70 %.

## [Color development speed and color disappearance speed]

[0041] Color development speed (ta) and color disappearance speed (tb) were measured as below.

35

T1 : transmittance in non-irradiation of ultraviolet light  
 T2 : transmittance in irradiation of ultraviolet light  
 ta : a time in which transmittance is changed from T1 to  $(T1+T2)/2$  by irradiation of ultraviolet light  
 tb : a time in which transmittance is changed from T2 to  $(T1+T2)/2$  by shielding irradiated ultraviolet light

40 [0042] Both ta and tb were determined by a curve of change of transmittance in maximum absorption wave length with the lapse of time.

## 45 Comparative Example 1

[0043] The synthetic resin laminate was obtained in the same experiment as in Example 1 except that the urethane was changed to solvent type one-liquid, Hamatai Y-7122-A, manufactured by Yokohama Gomu k.k., in Japan. The proportion of each component was shown in Table 1 and the evaluation results were shown in Table 2.

## 50 Examples 5 to 12

[0044] 1 % of Photochromic compound 3 to resin solid matter, 0.5 % of Photochromic compound 4 to resin solid matter were added to a solution of 15 g of a polyurethane precursor diluted with 13.6 g of an organic solvent (toluene 4.6 g, methylethyl ketone 1.8 g and ethyl acetate 7.2 g) in the same manner as in Example 1 and each Additives 1 to 4 was further added thereto in the blend proportion shown in Table 3 and dissolved and 1.6 g of the same curing agent as in Example 1 was added thereto and stirred.

[0045] The solution thus obtained was coated with a doctor blade of coating thickness 300  $\mu$ m, manufactured by Yoshimitsu Seiki k.k., in Japan on a polycarbonate film of thickness 300  $\mu$ m (trade name : IUPILON, manufactured by

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Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer. Another polycarbonate film of 300 µm was adhered thereto to make a sheet form and heat curing was performed at 70 °C for 3 days. The same evaluation as in Example 1 was performed for the synthetic resin laminate thus obtained. In the evaluation of light resistance, the evaluation was performed by changing the apparatus and further increasing ultraviolet light radiant intensity. The evaluation results were shown in Table 4. Further, when the samples thus prepared were exposed to sun light, they presented brown and when they were put in a dark place, color disappearance occurred.

## Organic Photochromic compound 3 :

[0046] 4- [4- (6-(4-morpholynyl) -3-phenyl-3H-naphtho [2,1-b]pyran-3-yl]phenyl]-morpholine

## Organic Photochromic compound 4 :

[0047] 1,3-dihydro-1,3,3,5,6(1,3,3,4,5)-pentamethylspiro(2H-Indole-2,3- [3H]-naphtho[2,b][1,4]oxazine)

Additive 1 : the same as in Example 1 bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate

Additive 2 : bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate

Additive 3 : bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate

+  
1-(methyl)-8- (1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate

Additive 4 : 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane

[0048] The [measurement of transmittance] and measurement and evaluation of [color development speed and color disappearance speed] was performed in the same manner as in Example 1.

## [Evaluation of light resistance]

[0049] As the evaluation, a UV lamp was irradiated for 5 minutes prior to light resistance test and after light resistance test and then contrast due to color development and color difference were measured and contrast retention percentage and color change degree in color disappearance in the light resistance test were calculated. Thus, light resistance was evaluated. In the light resistance test, an apparatus with a xenon lamp as the light source (apparatus name : SUNTEST CPS+, maker : manufactured by ATLAS) was used and an irradiance of 750 W/m<sup>2</sup> (300 to 800 nm) for 20 hours was applied. Further, the UV lamp had a single wave length of 360 nm in an ultramonochromatic light source (Nihon Bunko k.k., in Japan).

## ① Calculation of contrast retention percentage

[0050] It was calculated in the same method as in Example 1.

## ② Calculation of color change degree

[0051]

## color change degree

$$= [(L^*_{1,1} - L^*_{1,3})^2 + (a^*_{1,1} - a^*_{1,3})^2 + (b^*_{1,1} - b^*_{1,3})^2]^{1/2}$$

- a<sup>\*</sup><sub>1,1</sub> : a<sup>\*</sup> value prior to light resistance test (ultraviolet light non-irradiation)
- a<sup>\*</sup><sub>1,3</sub> : a<sup>\*</sup> value after light resistance test (ultraviolet light non-irradiation)
- b<sup>\*</sup><sub>1,1</sub> : b<sup>\*</sup> value prior to light resistance test (ultraviolet light non-irradiation)
- b<sup>\*</sup><sub>1,3</sub> : b<sup>\*</sup> value after light resistance test (ultraviolet light non-irradiation)

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## ③ Evaluation

## [0052]

5       O: After light resistance test, contrast is 70 % or above and color change degree is below 5 %.  
Δ: After light resistance test, contrast is below 70 % and color change degree is 5 % or above.

## INDUSTRIAL APPLICABILITY

10     [0053] In the formation of a polyurethane layer on a transparent synthetic resin surface, a polyurethane layer could be formed without impairing any photochromic performance by using specific two-liquid thermosetting polyurethane and mixing a polyurethane prepolymer, a curing agent and various additives including a photochromic compound in specific solvent and a transparent synthetic resin laminate with photochromism property to provide high availability could be produced efficiently by ensuring substantially non-solvent state thereof and then adhering another transparent synthetic resin and then performing heat cure. Further, a plastic lens with high photochromic performance and smooth photochromic layer could be obtained readily by using the laminate.

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Table 1

Polyurethane precursor	Curing agent	THF (Note 1)	Species of photochromic compound	Concentration of photochromic compound (g)	Additive (g)	Concentration of additive (%)
Example 1	15	3	8.3	1	2	1
	15	3	8.3	1	2	1
	15	3	8.3	2	2	1
	15	3	8.3	2	2	1
Comp. Bx. 1	30	—	—	1	2	1
	(Note 2)					

Note 1 : tetrahydrafuran

Note 2 : solvent type one-liquid

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Table 2

Photo- chromic layer	Thickness of color develop- ment wave length ( $\mu$ m)	Color in color absorp- tion wave length (nm)	Maximum transmittance in maximum absorption wave length ultraviolet light	Color in non- irradia- tion (%)	Color in irradia- tion (%)	Develop- ment speed (sec)	Appea- rance disapp- earance speed tb	Life
Example 1	177	blue	620	83	50	13	13	good
2	178	blue	620	83	58	13	13	good
3	181	yellow	440	87	65	10	10	good
4	179	yellow	440	88	65	10	10	good
Comp. Ex. 1	175	blue	620	90	52	23	26	good

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Table 3

Polyurethane precursor	Curing agent	Toluene MEK (Note 3) ethyl acetate	(g)	Photochromic compound			Additive	
				species	concentration (%)	species	concentration (%)	antioxidant
Example 5	15	1.6	13.6	3	1.0	2	3.0	—
				4	0.5			
Example 6	15	1.6	13.6	3	1.0	2	3.0	4
				4	0.5			3.0
Example 7	15	1.6	13.6	3	1.0	3	3.0	—
				4	0.5			
Example 8	15	1.6	13.6	3	1.0	3	3.0	4
				4	0.5			3.0
Example 9	15	1.6	13.6	3	1.0	1	3.0	—
				4	0.5			
Example 10	15	1.6	13.6	3	1.0	3	15.0	—
				4	0.5			
Example 11	15	1.6	13.6	3	1.0	3	15.0	4
				4	0.5			3.0
Example 12	15	1.6	13.6	3	1.0	—	—	—
				4	0.5			

Note 3 : methylethyl ketone

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Table 4

Example	Thickness of photochromic wave layer (μm)	Maximum absorption wave length (nm)	Transmittance in maximum absorption wave length	Color development	Color disappearance	Appearance			Life		
						Ultraviolet light speed	ta	tb	contrast	color change	degree
									retention	per-	cent
Example 5	133	460	84	63	13	15	good	72	3	○	
Example 6	140	460	84	65	14	16	good	74	2	○	
Example 7	137	460	85	61	14	16	good	70	4	○	
Example 8	128	460	84	67	14	16	good	73	3	○	
Example 9	136	460	85	65	13	15	good	43	7	△	
Example 10	132	460	85	63	14	16	good	51	4	△	
Example 11	135	460	84	66	14	16	good	56	3	△	
Example 12	138	460	85	67	13	15	good	34	10	△	

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## Claims

1. A transparent synthetic resin laminate with photochromism property consisting essentially of two transparent synthetic resin layers and a photochromic layer formed by curing a mixture of a two liquid polyurethane of a polyurethane prepolymer and a curing agent and a photochromic organic compound which is interposed between said two transparent synthetic resin layers.  
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2. The laminate according to claim 1, wherein said polyurethane prepolymer is a compound with an isocyanate group on both ends obtained from diisocyanate and polyol.  
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3. The laminate according to claim 1, wherein said polyurethane prepolymer is a compound derived from a prepolymer having a number average molecular weight of 500 to 5000 and a curing agent having a number average molecular weight of 500 to 5000.  
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4. The laminate according to claim 2, wherein said polyurethane prepolymer is a compound with an isocyanate group on both ends derived from diphenylmethane-4,4'-diisocyanate and polypropylene glycol.  
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5. The laminate according to claim 1, wherein said curing agent is a compound with a hydroxyl group on at least both ends obtained from diisocyanate and polyol.  
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6. The laminate according to claim 5, wherein said curing agent is a compound with a hydroxyl group on at least both ends derived from tolylene diisocyanate and polypropylene glycol.  
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7. The laminate according to claim 1, wherein said two-liquid polyurethane contains tertiary hindered amine light stabilizer.  
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8. The laminate according to claim 1, wherein said two-liquid polyurethane contains a tertiary hindered amine light stabilizer and an antioxidant containing three or above of hindered phenol.  
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9. The laminate according to claim 1, wherein said photochromic organic compound is a spiropyran compound, a spiroxazine compound or a naphthopyran compound.  
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10. The laminate according to claim 1, wherein each said two transparent synthetic resins are a polycarbonate resin, a polymethyl methacrylate resin or a polycarbonate resin and a polymethyl methacrylate resin.  
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11. The laminate according to claim 1, wherein said transparent resin is a sheet.  
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12. A process for producing a transparent synthetic resin laminate with photochromism property which comprises: coating a mixture of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent, a photochromic organic compound and a solvent on one side of a transparent synthetic resin sheet, then, removing the solvent from the mixture to a state not to contain substantially the solvent, then, adhering another transparent synthetic resin sheet to the coated side of said synthetic resin sheet, and then, curing the two-liquid polyurethane, thereby, forming a photochromic layer.  
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INTERNATIONAL SEARCH REPORT		International application No. PCT/JP01/02978
<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl' G02B 5/23, G02C 7/10, B32B 27/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl' G02B 5/23, G02C 7/10, B32B 27/40		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1940-1996 Tokoku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1991-2001 Jitsuyo Shinan Tokoku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 294056, A2 (Pilkington PLC), 07 December, 1988 (07.12.88), Full text; all drawings & GB, 6712210, A & JP, 2849386, B2 & US, 4889413, A & DE, 3888868, C & BR, 8802478, A & AT, 104066, T & ES, 2054804, T	1-12
A	JP, 4-226750, A (Nissan Motor Co., Ltd., et al.), 17 August, 1992 (17.08.92), Full text; all drawings (Family: none)	1-12
A	JP, 63-178193, A (Nippon Sheet Glass Company, Limited), 22 July, 1988 (22.07.88), Full text; all drawings (Family: none)	1-12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" documents published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 03 July, 2001 (03.07.01)		Date of mailing of the international search report 10 July, 2001 (10.07.01)
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP01/02978

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category*	Citation of document, with indication, where appropriate, of the relevant passages	
A	JP, 61-148048, A (Unitika Ltd.). 05 July, 1986 (05.07.92), Full text; all drawings (Family: none)	1-12

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